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Reaction pathways of glucose and fructose on Pt nanoparticles in subcritical water under a hydrogen atmosphere

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ABSTRACT

The reactivity profiles of glucose (Glc), fructose (Fru), and possible intermediate compounds treated with Pt nanoparticles protected by polyethyleneimine (Pt-PEI) were studied at 403–543 K in subcritical water under a hydrogen atmosphere of 5 MPa. Isomerization between Glc and Fru proceeded at the temperature as low as 403 K and was accelerated by Pt-PEI and H_2. The rate of isomerization from Glc to Fru in the presence of Pt-PEI and H_2 was approximately three times greater than the rate of the reverse reaction. Yields of sorbitol and mannitol were maximized at 443 K and decreased at higher temperatures. Under reaction temperatures of 483–543 K, Glc produced mainly 1,2-propanediol, 1,2-hexanediol, and ethylene glycol, while Fru yielded 1,2-propanediol, 1,2-hexanediol, and glycerol. The molar ratios of C3 compounds to the sum of C2 and C4 compounds in this temperature range were approximately 2:1–1.5:1 in the former and 3:1–4:1 for Fru, indicating that C3 compounds can be preferentially produced from Fru. The reactivity profiles of sorbitol, mannitol, and 1,2-hexanediol were examined in separated experiments at 483–543 K, and it was found that these linear C6 compounds were not converted to the previously mentioned C2–C4 diols and triols. This suggests that there is little possibility for Glc or Fru to form C2–C4 compounds via sorbitol, mannitol, or 1,2-hexanediol on the Pt catalyst, and it is likely that retro-aldol reactions of Glc and Fru are the major routes to these molecules. The temperatures necessary to conduct these reactions on Pt were much lower than those without Pt.

1. Introduction

Because of the impact of current technologies on global warming and the depletion of fossil fuels, development of effective methods to convert biomass into fuels and other valuable chemicals is a very important goal. Cellulose, a polymer constructed from glucose monomers, is a major component of wood and other plant-derived resources. Its conversion into useful chemicals by microorganisms, acid or alkaline solutions, and sub- or supercritical water has been widely studied [1–3]. The last method has gathered much attention due to its high dissolving power, high ionic product, and the use of an environmentally benign solvent. A variety of products were reported in sub- or supercritical water, including glucose (Glc) and its derivatives, fructose (Fru), erythrose, glyceraldehyde, pyruvaldehyde, and 5-hydroxymethyl-2-furfural. These compounds were produced through hydrolysis, dehydration, isomerization, retro-aldol reactions, and aldol condensations [3–5]. A few catalysts have also been applied to this reaction system; for example, Pt or Ru-based catalysts gave sorbitol and mannitol with moderate yields [6,7], sulfated active carbon was very effective for Glc formation [8,9], and Ni–W_2C/carbon was useful for the production of ethylene glycol [10,11].

It is widely accepted that cellulose would first react to form platform compounds such as Glc, Fru, sorbitol, and mannitol, and these compounds would subsequently be converted to smaller molecules containing 2–5 carbon atoms. Elucidation of the reaction pathways available to cellulose, the first stage in this process, is important, but this is currently quite difficult due to the complexity of the system. Therefore, many studies have focused on reactions of Glc, with or without catalysts, in sub- and supercritical water. For example, isomerization between Glc and Fru has been reported to be accelerated by basic [12–15] or supercritical conditions [16]. Retro-aldol reactions of Glc were observed to proceed in supercritical water, producing glyceraldehydes in 64% yield [17]. The methyl ester of lactic acid was also obtained in 64% yield from Glc when treated with Sn-beta zeolite at 422 K in methanol [18]. In addition, hydrogenation of Glc has been investigated on Ru, Ni [19,20], and Cu [21] catalysts, forming sorbitol with selectivities in the range of 85–98%.

As mentioned above, the reactions of cellulose and Glc have been widely studied in sub- and supercritical water with or without catalysts, but most of the studies conducted so far have focused on obtaining one or more target compounds with high yields. In contrast, not much effort has been made to provide a more com-

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prehensive knowledge of the reaction pathways available to Glc; in particular, few systematic studies on the catalytic hydrogenation of Glc have been conducted so far, to our knowledge. This study was therefore devoted to revealing reaction pathways from Glc to various products on a Pt catalyst under subcritical conditions. Isomerization between Glc and Fru and the reactivity of possible intermediate compounds were also studied. In our preliminary experiments, the catalytic activity for conversion of Glc in water at 503 K was found to decrease in approximately the following order: Pt protected by polyethyleneimine (Pt-PEI), Pt protected by polyvinylpyrrolidone, Pt supported on silica, Pt supported on alumina. Pt-PEI was thus employed as the catalyst for this study due to its high hydrogenation activity, high dispersibility in water, and relatively inert support polymer [22].

2. Experimental

2.1. Materials

All chemicals were obtained commercially and used without any purification. Pt-PEI nanocolloid catalyst was obtained from Tanaka Kikinzoku Kogyo K. K. The donated reagent contained Pt nanoparticles with diameters of 3–5 nm in water (0.5% Pt and 1.0% PEI by weight). The amount of PEI introduced by the catalyst was very small relative to the reactants; it was therefore not included in calculations of carbon balance before and after the reactions.

2.2. Experimental method and analyses of products

All catalytic experiments were conducted in a 100 mL stainless (SUS-316) autoclave (OM Lab-Tech Co. Ltd., MMJ-100). Unless otherwise stated, 0.48 g of substrate (16.0 mmol of carbon atoms in the case of Glc), 1 g of a Pt-PEI aqueous dispersion (containing 5 mg Pt) and 60 g of ion-exchanged water were charged into the autoclave. Hydrogen was then introduced into the vessel at ambient temperature until the pressure reached 5.0 MPa (ca. 120 mmol H_2). The mixture was stirred at 1100 rpm by agitating blades and heated to the desired temperature (403–543 K). Due to the heat capacity of the vessel and the reaction solution, 20–25 min of heating was required to reach the desired temperature. “Reaction time” in this study meant the time between reaching the target temperature and starting the cooling treatment. Approximately 1 h was required to cool the reaction vessel. The pressures in the vessel were 6–11 MPa at 403–543 K.

Products and unreacted substrates were analysed by gas chromatography with a mass spectrometer (GC–MS; Shimadzu, GCMS-QP2010) or a flame ionization detector (GC-FID; Shimadzu, GC2014). The amounts of various diols were determined by a Stabilwax column (Restek) in which acetonitrile was employed as an internal standard. Yields of sugars and sugar alcohols were measured by high performance liquid chromatography with a refractive index detector (HPLC; Shimadzu, RID-10A). An SP0810 column (Shodex) was employed at 343 K. Total amounts of organic carbons dissolved in water were determined by a total organic carbon analyzer (TOC; Shimadzu, TOC–V_{CNS}). Ratios of 1,2-propanediol enantiomers were analysed by GC-FID with an RT-μDEXse capillary column (Restek) after acetylation of the reaction mixture was carried out with acetic anhydride and pyridine at room temperature.

The yields of products (%) were calculated based on carbon balance.

$$\text{Yield} = 100 \times \frac{\text{mol product} \times \text{number of carbon atoms in product}}{\text{mol substrate} \times \text{numbers of carbon atoms in substrate}}$$

It should be noted that substantial efforts were devoted to quantitative measuring of the product distributions by using GC, HPLC and MS, but significant amounts of products could not be determined due to bad resolution in the HPLC chromatograms. The insufficient analyses obviously resulted in poor mass balances and disrupted reaction pathways for most experiments as shown in the following results.

3. Results and discussion

3.1. Reactions of Glc and Fru with or without Pt-PEI

Typical product distributions for reactions of Glc and Fru at 503 K are summarized in Table 1. Even after 1 min of reaction without the catalyst, only 20–2% of the substrate remained, indicating rapid reaction of Glc and Fru under subcritical conditions; however, reactions during heating and cooling procedures were also included. Without Pt-PEI, the TOC values after reaction times of 1 and 180 min were 93 and 59% for Glc and 97 and 82% for Fru. Thus, the values were approximately 100% after 1 min but decreased to 59 and 82%, respectively, after 180 min. Sticky yellowish compounds were observed in reactions of both Glc and Fru after 180 min, suggesting that the decreases in TOC values may be due to oligomerization or condensation reactions of the substrates or products. In the 1 min reactions of Glc and Fru, 5-hydroxymethyl-2-furfural was a major product, but amounts of this compound gradually decreased with reaction time and almost disappeared at 180 min. Facile production of 5-hydroxymethyl-2-furfural from sugars [23–25] and self- and cross-polymerization of 5-hydroxymethyl-2-furfural and other products in an acidic aqueous solution [26] have already been reported in many studies. This might be the reason for the decrease in TOC values and the formation of sticky compounds.

The product distributions were greatly changed in the presence of Pt-PEI. The TOC values were over 96% in all reactions irrespective of the reaction time. The major products were 1,2-propanediol, ethylene glycol, 1,2-hexanediol, 1,2-butanediol, and hydroxyacetone. In contrast to the reactions without Pt-PEI, no production of 5-hydroxymethyl-2-furfural was observed in this case. Sorbitol and mannitol were also observed in the 1 min reactions. The product distributions clearly indicated that Pt-PEI catalyzed C–C cleavage in the substrates. The most common product in the reactions of both Glc and Fru was racemic 1,2-propanediol. The catalytic conversion of Glc to 1,2-propanediol has already been reported; for example, a 60% yield was obtained by using CuO/Cr_2O_3 and hydrogen in subcritical ethanol [21], and a 29% yield was obtained using Ru/C and hydrogen in subcritical water with a phosphate buffer [27]. It is noteworthy that the present system gave 1,2-propanediol in 24–28% yield without any organic solvent or salt. Several other interesting observations will be discussed in more detail below. The yields of 1,2-hexanediol from Glc were almost the same as those from Fru. The amounts of 1,2-hexanediol at 180 min were greater than those at 1 min, indicating its formation from some undetermined intermediate product(s). The yields of ethylene glycol and 1,2-butanediol from Glc were higher than those from Fru. The total yields of all diols in the reactions of Glc and Fru were approximately 50% after the 180 min reactions.

Next, the product distributions for the reactions of Glc and Fru on Pt-PEI in the presence of hydrogen were studied over the temperature range of 403–543 K (Fig. 1). No Glc was observed at 463 K or above. Fru was produced below 443 K, and the yields of sorbitol and mannitol were maximized at 443 K. Higher temperatures led to increased amounts of diols and glycerol. The maximum yield of 1,2-hexanediol was observed at 463 K, and 1,2-propanediol and ethylene glycol production was maximized at 523 K. Isomerization from Fru to Glc was observed below 443 K (Fig. 1B), but the extent of isomerization was less than that from Glc to Fru when Glc was used as a starting material (Fig. 1A). The yields of sorbitol and mannitol were maximized at 443 K for Fru as well. At

Table 1
Product distributions after reactions of Glc and Fru at 503 K.[a]

Run	Sub.	Pt-PEI (g)	Time (min)	Conv. (%)	TOC (%)	Yield[b,c] (%)										
						Sor	Man	HMF	HD	BD	PD	GC	HA	LA	EG	AA
1	Glc	0	1	80	93	0	0	34	0	0	0	0	1	0	0	1
2	Glc	0	15	97	84	0	0	31	0	0	0	0	1	2	0	1
3	Glc	0	30	>99	81	0	0	25	0	0	0	0	1	2	0	1
4	Glc	0	60	>99	76	0	0	15	0	0	0	0	1	2	0	1
5	Glc	0	180	>99	59	0	0	2	0	0	0	0	1	2	1	1
6	Glc	1	1	>99	98	14	8	0	9	3	11	3	1	0	6	0
7	Glc	1	180	>99	99	1	2	0	12	7	24	3	0	0	9	0
8	Fru	0	1	98	97	0	0	27	0	0	0	0	15	5	0	5
9	Fru	0	180	>99	82	0	0	0	0	0	0	0	8	4	0	3
10	Fru	1	1	>99	100	8	0	0	7	2	13	9	11	0	4	0
11	Fru	1	180	>99	96	2	2	0	11	6	28	9	1	0	5	0

[a] Reaction conditions were described in Section 2.

[b] Product yields were calculated on a carbon basis, and values of 0 mean yields less than 0.5%.

[c] Substrates and products include glucose (Glc), fructose (Fru), sorbitol (Sor), mannitol (Man), 5-hydroxymethylfurfural (HMF), 1,2-hexanediol (HD), 1,2-butanediol (BD), 1,2-propanediol (PD), glycerol (GC), hydroxyacetone (HA), lactic acid (LA), ethylene glycol (EG), and acetic acid (AA).

483–543 K, 1,2-propanediol, 1,2-hexanediol, and glycerol were the main products.

The isomerization between Glc and Fru and the reactivity of sorbitol and mannitol will be discussed in more detail in the next section. It was revealed here that Glc and Fru have fairly different reactivity patterns due to structural differences between the aldose and the ketose. It should be noted that at 403 K, a few percent of the Fru starting material resulted in dihydroxyacetone. This presumably involves C–C cleavage between α- and β-carbon of the carbonyl group via a retro-aldol reaction [17].

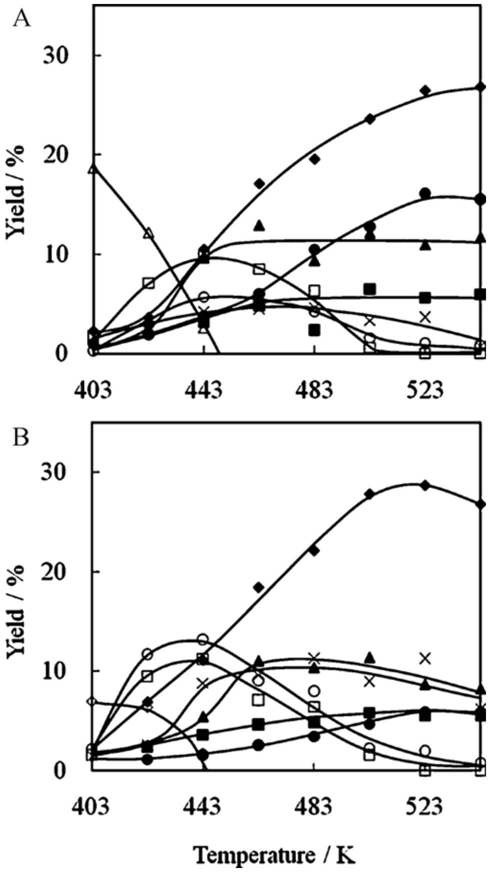

Fig. 1. Temperature dependencies of product distributions for Glc (A) and Fru (B). Glc (open diamond), Fru (open triangle), sorbitol (open square), mannitol (open circle), 1,2-hexanediol (closed triangle), 1,2-butanediol (closed square), glycerol (cross), 1,2-propanediol (closed diamond), ethylene glycol (closed circle). Reaction conditions: 0.48 g Glc or Fru, 60 g water, 1 g Pt-PEI dispersion, 5 MPa H_2 (initial pressure), and 180 min.

3.2. *Isomerization of Glc or Fru and reactivity of sorbitol, mannitol, 1,2-hexanediol, and the others*

The isomerization between Glc and Fru was examined at 403 K and summarized in Table 2. Note that this reaction temperature is lower than the reactions in Table 1, which were conducted at 503 K, to trace only the isomerization reactions. Three observations were made concerning the effects of differing substrates, the presence or absence of Pt-PEI, and the choice of H_2 or Ar atmospheres. Firstly, the isomerization between Glc and Fru was indeed promoted by the addition of Pt catalyst and H_2. In particular, it should be noted that the presence of H_2 promoted the isomerization even though there is no difference between molecular formulas of Glc and Fru. Secondly, in the presence of Pt and H_2, the rate of isomerization from Glc to Fru (Run 3) was approximately three times higher than the rate of the reverse reaction (Run 7). Thirdly, although both Glc and Fru produced sorbitol, mannitol was generated only from Fru.

The effect of H_2 and Ar on the time course of Glc isomerization at 403 K was studied, and the results are shown in Fig. 2A and B. The extent of isomerization was greater with H_2 atmosphere than with Ar one, in agreement with the results in Table 2. Two types of reactions were observed; rapid reactions took place in the first 30 min, and slower reactions occurred at around 50–180 min. In the latter time period, the amounts of sorbitol and mannitol gradually increased, as shown in Fig. 2A, indicating the reaction sequence of Glc → Fru → mannitol in addition to Glc → sorbitol, as suggested in the previous section. In the absence of hydrogen (Fig. 2B), very little reactivity was observed during the corresponding time period.

Changes in pH values over times were measured with or without Glc in the presence (Fig. 2C) or absence of H_2 (Fig. 2D). The initial pH value of an aqueous solution containing only Pt-PEI was 7.0–7.3 at ambient temperature. For reasons that are not fully clear, this value increased to 8.5 upon heating to 403 K for 1 min without Glc. In the absence of Glc, pH values at 403 K were constant over 180 min under both H_2 and Ar, as shown in Fig. 2C and D (closed diamond). Upon addition of Glc, the initial pH values was decreased somewhat, with a smaller drop observed in H_2 (ca. 8.1) than in Ar (6.8). The subsequent reactions of Glc caused significant decreases in the pH values. Although the absolute pH value for H_2 (6.0) was much higher than that for Ar (4.6), the overall decrease was similar in H_2 (8.1 → 6.0) and Ar (6.8 → 4.6), which would be caused by the formation of various acidic products. The difference between

Table 2
Effects of Pt-PEI and hydrogen on isomerizations between Glc and Fru at 403 K.

Run	Substrate	Pt-PEI[a] (g)	Gas phase	Yield[b] (%)			
				Glc	Fru	Sorbitol	Mannitol
1	Glc	0	H_2	(87)[c]	7	2	0
2	Glc	0	Ar	(99)[c]	2	0	0
3	Glc	1	H_2	(69)[c]	19	2	0
4	Glc	1	Ar	(84)[c]	11	0	0
5	Fru	0	H_2	3	(85)[c]	0	0
6	Fru	0	Ar	0	(93)[c]	0	0
7	Fru	1	H_2	7	(69)[c]	2	2
8	Fru	1	Ar	2	(91)[c]	0	0

[a] Pt-PEI contained 0.5 wt% Pt and 1.0 wt% polyethyleneimine. Reaction conditions: 0.48 g substrates, 60 g water, 403 K, 180 min, and 5 MPa H_2 or Ar.
[b] Abbreviation of compounds is the same as in Table 1. Yields were calculated on a carbon basis.
[c] The numerical values in parentheses are amounts of remaining substrate.

the initial pH values in H_2 and Ar may be due to the coordination of hydrogen atoms onto Pt particles. It is well known that nitrogen atoms in PEI coordinate and stabilize the Pt clusters [28]. The hydrogen atoms originating from H_2 could adsorb on the surface of the Pt nanoparticles, which would result in the release of PEI from the Pt clusters. The resulting free PEI molecules might then react with water molecules to produce OH^- ions in the solution and increase the initial pH value.

As shown in Fig. 1, the yields of sorbitol, mannitol, 1,2-hexanediol, 1,2-butanediol and glycerol were maximized in the middle temperature range, suggesting that they might be intermediates in the hydrogenation reactions. Therefore, their reactivity was investigated and the results are summarized in Table 3. No conversion of sorbitol was observed at 483 K (Run 1) but a higher reaction temperature resulted in its disappearance (Runs 2 and 3). Small amounts of mannitol and diols were obtained at these temperatures, but the products observed in Fig. 1 were not detected. Some cyclic compounds were observed in mass spectrometer analyses, though their amounts were not determined. The selective conversion of sorbitol to ethylene glycol on Ru catalysts [29,30] has been reported, but this was not the case for Pt-PEI. It was further confirmed that mannitol showed similar reactivity to that of sorbitol, though no cyclic compound was observed. On the other hand 1,2-hexanediol and 1,2-butanediol remained unchanged at 503–543 K. These results indicate that the C2–C4 diols and triol produced in the reaction of Glc or Fru on Pt-PEI (Fig. 1) did not result from reactions of sorbitol, mannitol, or the other linear C4–C6 diols.

The reaction of glycerol gave 1,2-propanediol with 80% selectivity at 503–543 K. The conversion of glycerol to 1,2-propanediol has already been reported using various catalysts [31]. The 80% selectivity on Pt-PEI is comparable to values reported for Pt/C by Degussa and for copper-chromate by Sud-Chemie [31].

3.3. *Reaction pathways from Glc to the various products*

On the basis of the above findings, the reaction pathways of Glc to various products will be discussed here. The reaction routes suggested here are summarized in Fig. 3, which includes isomerization of Glc or Fru and retro-aldol reactions similar to those suggested for super critical water [3,17,18,32]. The isomerization between Glc and Fru was confirmed for the present conditions, and the reaction rate from Glc to Fru was approximately three times higher than that of the reverse reaction at 403 K in the presence of Pt-

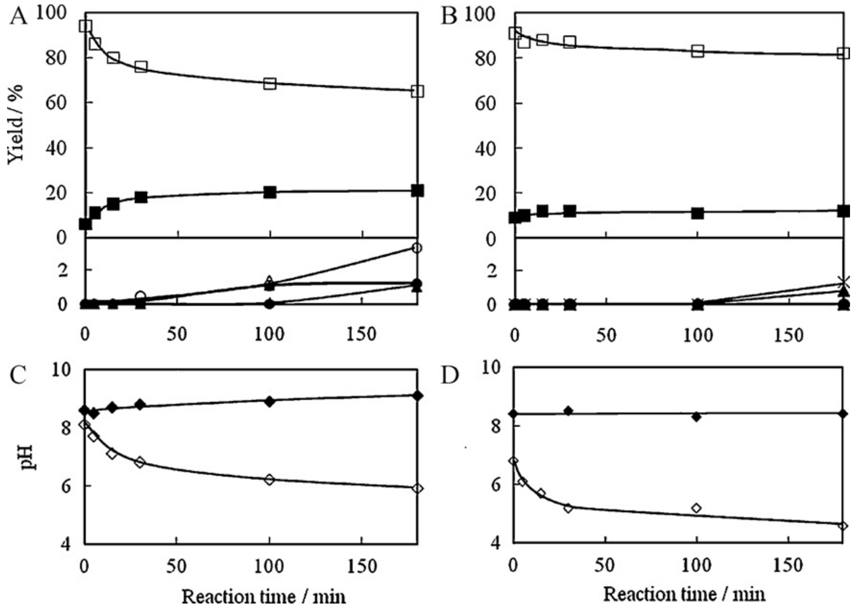

Fig. 2. Time courses for isomerization of Glc in H_2 (A) and Ar (B), and changes in solution pH values with (open diamond) or without Glc (closed diamond) in H_2 (C) and Ar (D). Glc (open square), Fru (closed square), sorbitol (open circle), mannitol (closed circle), hydroxyacetone (closed triangle), dihydroxyacetone (open triangle), 5-hydroxymethyl-2-furfural (star). Reaction conditions: 0.48 g Glc, 60 g water, 1 g Pt-PEI dispersion, 5 MPa H_2 or Ar (initial pressure), and 403 K.

Table 3
Reactivity of sorbitol, mannitol, 1,2-hexanediol, 1,2-butanediol, and glycerol on Pt-PEI in H_2.

Run	Substrate	Temp. (K)	Yield[a] (%)						
			Sor	Man	HD	BD	GC	PD	EG
1	Sorbitol	483	(100)[b]	0	0	0	0	0	0
2	Sorbitol	503	(89)[b]	2	0	0	0	1	1
3	Sorbitol	543	(55)[b]	3	1	2	0	5	4
4	Mannitol	483	2	(92)[b]	0	3	0	2	1
5	Mannitol	503	5	(76)[b]	0	4	0	2	1
6	Mannitol	543	7	(60)[b]	1	4	0	2	1
7	1,2-Hexanediol	503	0	0	(100)[b]	0	0	0	0
8	1,2-Hexanediol	543	0	0	(99)[b]	0	0	0	0
9	1,2-Butanediol	503	0	0	0	(100)[b]	0	0	0
10	1,2-Butanediol	543	0	0	0	(99)[b]	0	0	0
12	Glycerol	503	0	0	0	0	(95)[b]	4	0
13	Glycerol	543	0	0	0	0	(70)[b]	24	3

[a] Pt-PEI contained 0.5 wt% Pt and 1.0 wt% polyethyleneimine. Reaction conditions: 0.48 g substrates, 60 g water, 403 K, 180 min, and 5 MPa H_2 or Ar. Yield was calculated on a carbon basis. Abbreviation of compounds is the same as in Table 1.

[b] The numerical values in parentheses are amounts of recovered substrate.

PEI and H_2. 5-Hydroxymethyl-2-furfural was only produced in the absence of Pt-PEI and H_2, so it is not described in the figure. This is consistent with the reports that 5-hydroxymethyl-2-furfural is produced only in acidic solutions or when using acid catalysts [2–5]. Sorbitol and mannitol were obtained at temperatures in the range 423–483 K, but they were not intermediates for the formation of C2–C4 compounds, as shown in the previous section.

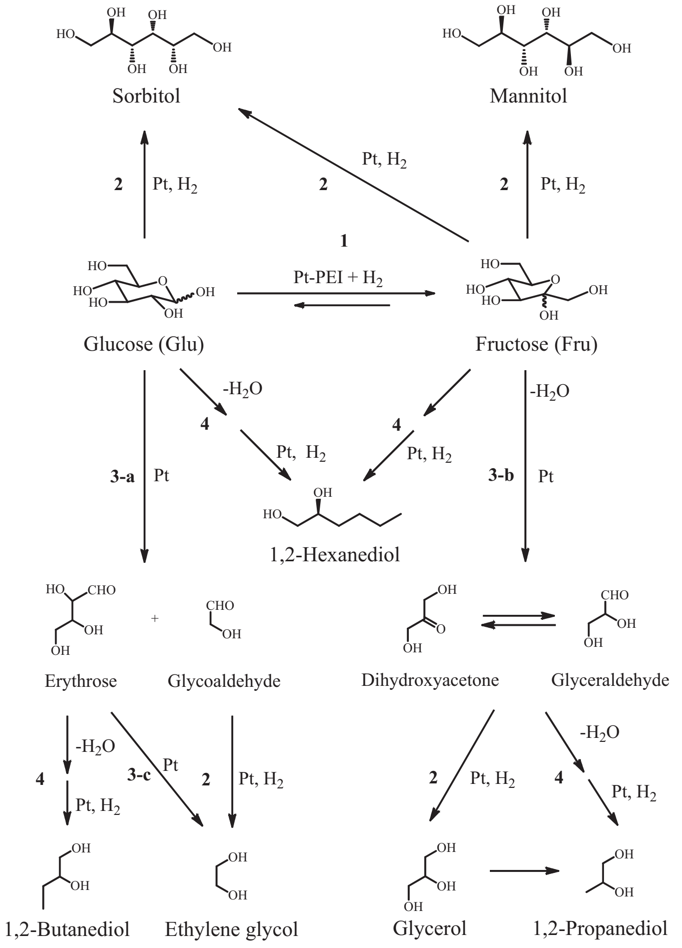

Fig. 3. Suggested pathways for hydrothermal reactions of Glc on Pt-PEI in H_2. The numerical value indicates the type of reaction; 1 indicates isomerization, 2 is hydrogenation, 3-a, 3b, 3c are retro-aldol reactions, and 4 is dehydration and hydrogenation.

Based on the results in Fig. 1, the amount of C3 compounds and the sum of C2 and C4 compound are plotted as a function of reaction temperature in Fig. 4. The molar ratios of C3 to C2 + C4 compounds in the Glc reaction were roughly 2:1–1.5:1 while ratios for Fru were 3:1–4:1. The amounts of C3 compounds from Glc were always smaller than those from Fru, clearly indicating that the C3 compounds could be produced more easily from Fru in this reaction system. One can suggest the occurrence of retro-aldol reactions for Glc and Fru under the present conditions. Namely, substrate activated by the catalyst would result in C–C bond scission to yield C4 and C2 compounds from Glc and C3 compounds from Fru. The observation of dihydroxyacetone in the reaction also supports the indicated reaction routes. Erythrose and glycoaldehyde were not detected, presumably due to their rapid hydrogenation to 1,2-butanediol and ethylene glycol. The fact that the product distributions in Fig. 1 are not the same suggests that Glc and Fru do not fully equilibrate under the present reaction conditions. It has already been reported that in the absence of catalyst, the dehydration reactions of Glc and Fru become significant at 523–623 K and the contribution from retro-aldol reactions become predominant at 673–773 K [16]. It is reasonable to assume that similar reac-

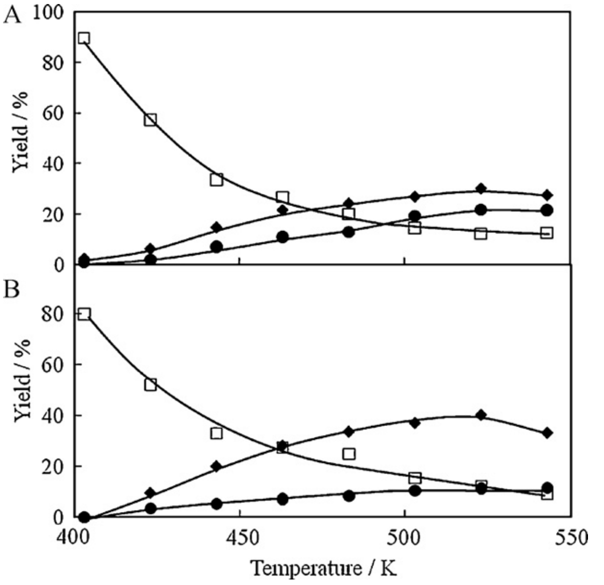

Fig. 4. Total amount of C2 and C4 products (closed circle), C3 products (closed diamond), and C6 products (open square) from Glc (A) and Fru (B) as a function of reaction temperature. All data were calculated based on the results shown in Fig. 1.

tions proceed at much lower temperatures in the presence of Pt and H_2.

4. Conclusions

Glc and Fru were reacted with Pt-PEI under H_2 at various temperatures. Although the identities of products were almost the same in both reactions, the distributions were fairly different. The isomerization of Glc to Fru proceeded faster than the reverse reaction, especially in the presence of Pt catalyst and H_2. At around 443 K, sorbitol and mannitol were the major products, but these were not intermediates in the formation of the C2–C4 products observed at higher temperatures. Product distributions of C2–C4 compounds at 463–543 K suggested the occurrence of retro-aldol reactions undergone by Glc and Fru and subsequent hydrogenations of the resultant intermediate compounds on the Pt catalyst. Glc gave mainly C2 and C4 compounds, while Fru produced the C3 compounds. The present results show that the product distribution was determined by the reaction temperature, the kind of catalyst, and the atmosphere (H_2 or Ar). It should be noted that the isomerization between Glc and Fru was promoted by H_2 even though they are isomers. These results are potentially significant to the future improvement of yield and selectivity in biomass conversions.

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